Thermal expansion and the equation of state of Ir and Rh

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Abstract

The simplest anharmonic characteristics of Ir and Rh are discussed in the framework of a previously developed simple pseudopotential model which describes the elastic moduli, phonon spectra and the lattice heat capacity in the harmonic approximation of these metals succesfully. The microscopic Gruneisen parameters, the dependences of the elastic moduli on pressure, the coefficient of thermal expansion and the equations of state at the finite temperatures have been calculated. The *ab initio* calculations of the energy-band structure and the equation of state for Ir at $T = 0$ have been done to test the model for adequacy at high pressures. The values of different contributions (zero-point oscillations, quasiharmonic, etc.) in the considered thermodynamic characteristics of Ir and Rh are discussed.

§1. Introduction

As it is stated in the literature (Gornostyrev *et al* 1994, Ivanov *et al* 1994, Katsnelson *et al* 1996, hereinafter referred to as I), Ir and its analogue Rh are set off from other FCC metals because of some distinctive features of their physical properties: unusual deformation-induced failure, peculiar defect structure, specific temperature dependence of the effective Debye temperature, etc. Moreover, the situation is not trivial because in the case of Ir, unlike the most, if not all of the other FCC metals a rather broad range of properties (elastic moduli, phonon spectra and lattice heat capacity) can be described in terms of a simple pseudopotential model (see I and references therein). Even in *sp*-metals the situation is less favorable: to describe the elastic moduli of Ca allowance must be made for the singular contributions to energy which result from the proximity of the Fermi surface and the faces of the Brillouin zone (Katsnelson *et al* 1990), whereas for Al it is necessary to take into account the contributions of three body forces. Nevertheless, in describing the phonon spectra of Al it is impossible to attain an accuracy

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identical to that for Ir (Browman *et al* 1971, Fomichev *et al* 1990). In Ir the contribution of three body interactions proves to be small (Greenberg *et al* 1990). As a whole, it turns out that surprising as it may seem, Ir is probably exceeded in the accuracy of the psedopotential description of the lattice properties only by alkali metals. This gives hope that the theory can be used to predict those lattice properties of Ir for which the experimental data are scanty or absent, such as thermal expansion or the equation of state at different temperatures. To be sure, the pseudopotential model is oversimplified. Therefore, where it is possible, the model predictions should be tested against either the experiment or the results of the *ab initio* band calculations. Despite the fact that no simple model can completely substitute the *ab initio* calculations, to obtain a sufficiently reliable physical information about the complex properties of metals even with the help of a model approach appears to be of interest. At the same time, fully *ab initio* calculations of the phonon contributions to the thermodynamical properties of metals seem for the present to be impossible (or, in any case, are rather cumbersome). Therefore, the use of the pseudopotential model for these purposes, where it is possible seems to be justified. This paper presents the results of the calculations of the coefficient of thermal expansion at finite temperatures, and the dependence of the elastic moduli on pressure in terms of the pseudopotential model developed previously for Ir and Rh (see I). To understand to what extent the simple model used is reliable at high pressures the electron energy spectrum of Ir and its equation of state at $T = 0$ were calculated *ab initio* . The results of the calculations show that the equation of state calculated in the framework of the pseudopotential model seems to be sufficiently reliable.

§2. THERMAL EXPANSION AND GRUNEISEN PARAMETERS OF IR AND RH

In calculating the thermal expansion and the Gruneisen parmeters $\gamma(T)$ at finite temperatures as well as the dependencies of the elastic moduli on pressure $B_{ik}(p)$ use was made of the pseudopential model constructed in I and giving the optimal description of the phonon spectra. The results of the calculations in terms of an earlier model (Ivanov *et al* 1994) are given for comparison. The local pseudopotentials $V_{ps}(q)$ used in the two models are closely similar. However a slight change in the form of $V_{ps}(q)$ was made in I to describe better the phonon spectra. The screening function was taken in both cases in the Geldart and Taylor (1970) approximation (see, in more detail, Greenberg *et al* 1990). The temperature dependence of the volume

per atom $\Omega(T) \equiv \Omega_0 + \Delta\Omega(T)$ ($\Omega_0 = \Omega(T = 0)$), the coefficient of thermal expansion

$$\alpha_p = \frac{1}{\Omega}\left(\frac{\partial\Omega}{\partial T}\right)_p \tag{1}$$

and the Gruneisen parameter $\gamma(T)$ are determined by the following expressions (Vaks *et al* 1978):

$$\frac{\Delta\Omega(T)}{\Omega_0} = -\frac{p_{ph}(T)}{B_T}, \tag{2}$$

$$\alpha_p = \frac{1}{\Omega B_T}\sum_\lambda \left(\frac{\hbar\omega_\lambda}{T}\right)^2 N_\lambda(1 + N_\lambda)\gamma_\lambda \tag{3}$$

$$\gamma(T) = \frac{\Omega B_T \alpha_p}{C_V(T)} = \frac{\sum_\lambda \left(\dfrac{\hbar\omega_\lambda}{T}\right)^2 N_\lambda(1 + N_\lambda)\gamma_\lambda}{\sum_\lambda \left(\dfrac{\hbar\omega_\lambda}{T}\right)^2 N_\lambda(1 + N_\lambda)} \tag{4}$$

where

$$p_{ph} = \frac{1}{\Omega}\sum_\lambda \hbar\omega_\lambda N_\lambda \gamma_\lambda \tag{5}$$

is the phonon pressure; $\lambda \equiv \mathbf{q}\nu$, $\mathbf{q}$ is the phonon wave vector (sweeping the Brillouin zone); ν is the branch number; ω_ν is the phonon frequency;

$$\gamma_\lambda = -\frac{\partial\ln\omega_\lambda}{\partial\ln\Omega} \tag{6}$$

are the microscopic Gruneisen parameters;

$$N_\lambda = \frac{1}{\exp\dfrac{\hbar\omega_\lambda}{T} - 1}, \tag{7}$$

B_T is the bulk modulus at a constant temperature; $C_V(T)$ is the phonon heat capacity at a constant volume. The microscopic Gruneisen parameters are calculated by the formula

$$\gamma_\nu(\mathbf{q}) = -\frac{\Omega}{2\omega_{\nu\mathbf{q}}^2}\sum_{\alpha\beta}(e_{\nu\mathbf{q}}^\alpha)^*\frac{\partial D_{\alpha\beta}(\mathbf{q})}{\partial\Omega}e_{\nu\mathbf{q}}^\beta \tag{8}$$

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where D is the dynamic matrix; $\mathbf{e}_{\nu\mathbf{q}}$ are the polarization vectors; α and β are the Cartesian indices. In our calculations allowance was also made for the quasiharmonic corrections:

$$\alpha = \alpha_1 \left[1 - \left(\frac{\Delta\Omega}{\Omega} \right)_1 \frac{\partial \ln B}{\partial \ln \Omega} \right]$$

$$\frac{\Delta\Omega}{\Omega} = \left(\frac{\Delta\Omega}{\Omega} \right)_1 \left[1 + \left(\frac{\Delta\Omega}{\Omega} \right)_1 \left(1 - \frac{\partial \ln B}{\partial \ln \Omega} \right) \right] \tag{9}$$

where index "1" means the corresponding expression taken in the lowest order of anharmonicities. The procedure of calculating the thermal expansion of metals and its related quantities was discussed in more detail in Vaks *et al* 1978.

The results of the calculations are presented in figs. 1–4 and table 1. First of all, it should be noted once more that $\gamma_\nu(\mathbf{q})$ vary essentially over the Brillouin zone. This indicates again that the Gruneisen approximation $\gamma_\nu(\mathbf{q}) = const$ is completely unsuited for actual systems. As the temperature increases the macroscopic Gruneisen parameter $\gamma(T)$ reaches quickly (at $T \geq 0.1\Theta$, where Θ is the Debye temperature) a constant high temperature value. Alkali metals exibit the analogous behavior (Vaks *et al* 1978). However, unlike alkali metals having $\gamma \approx 1$, in Ir and Rh, as in majority of transition metals, $\gamma \approx 2$. Note also that the calculated values of $\gamma(T)$ are rather highly sensitive to the form of the pseudopotential used (compare the different curves in figs 3b and 4b).

§3. Equation of states. Used formulas and approximations

The equation of state for a metal, that is, the dependence of the pressure p on Ω and T is determined by the expression

$$p(\Omega, T) = p_0(\Omega) + p_{zp}(\Omega) + p_{ph}(\Omega, T) + \Delta p_e(\Omega, T) \tag{10}$$

where

$$p_0(\Omega) = -\frac{\partial E(\Omega)}{\partial \Omega}, \tag{11}$$

$E(\Omega)$ is the total energy of the crystal at $T = 0$;

$$p_{zp} = -\frac{\partial}{\partial \Omega} \sum_\lambda \left(\frac{\hbar\omega_\lambda}{2} \right) = \frac{1}{2\Omega} \sum_\lambda \hbar\omega_\lambda \gamma_\lambda \tag{12}$$

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is the pressure relating to the zero-point energy; p_{ph} is the phonon pressure (5);

$$\Delta p_e = \frac{\pi^2}{6} T^2 \frac{\partial N(E_F)}{\partial \Omega} \qquad (13)$$

is the temperature dependent contribution to the electron pressure; $N(E_F)$ is the density of states at the Fermi level E_F. We shall neglect the anharmonic contributions having the same order of magnitude as the deviation of the $\Delta p_e(T)$ from the "low-temperature" $(T \ll E_F)$ expression (13). Generally speaking, the allowance for the contribution of the zero-point vibrations $p_{zp}(\Omega)$ to the equation of state in the scheme with a pseudopotential whose parameters are fitted, among other things to the condition $\Omega = \Omega^{exp}$ at $p = 0$ requires to refit the parameters. However the results of Vaks *et al* 1977 show that even in metals as light as Li and Na such refitting is not very essential. In addition, in transition metals, in particular in Ir, the choice of the value for the effective charge is not quite unumbiguous, and strictly speaking, Z can be dependent of Ω ($Z \equiv 1$ in alkali metals). Because we ignore this knowingly more important effect, the results obtained in refitting the pseudopotential parameters with allowance for p_{zp} are not presented. The direct calculation shows that that the change in the results with such a refitting is actually small.

In calculating the major contribution to the pressure $p_0(\Omega)$ by (11) in the framework of the pseudopotential model for the energy $E(\Omega)$, use was made of the expression derived in the second order of the perturbation theory from a pseudopotential with the exchange-correlation energy according to analitical approximation (Perdew and Zunger 1981) of the results of the calculation by the quantum Montne-Carlo method (Ceperly and Alder 1980). For more details see Greenberg *et al* 1990. The *ab initio* calculations of the band structure and the total energy at different Ω were done by the augmentned plane wave method. The detailed procedure of these calculations is described by Sigalas *et al* 1992 and Sigalas and Papaconstantopulos 1994.

§4. Equation of state. Results of calculations

The strict calculation of equation of state for a metal by Eq. (10) is rather difficult. Whereas the electron contributions p_0 and Δp_e can be calculated form "the first principles", the calculation of the phonon contributions p_{zp} and p_{ph} in the fully "first- principle" approach is a very cumbersome procedure, and no corresponding results are known to us at that time. For this

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reason, to calculate the phonon contributions to pressure requires to use some model concepts.

We'll discuss first the results of the $T = 0$ calculations. Fig. 5 shows the values of $p_0(\Omega)$ calculated in the framework of the pseudopotential model and the band approach that we used. It is seen that the difference of the two curves is not too great, at least, at moderate pressures. The reason is that the values of the bulk modulus: 3.76 Mbar calculated with the used variant of the band theory (Sigalas *et al* 1992) and 2.93 Mbar in the pseudopotential model (see I) do not differ too much.

Table 2 lists the contribution of the zero point vibrations to the equation of state at $T = 0$. It is seen that this contribution is negligible. The results of the calculation of the phonon pressure in the pseudopotential model are shown in figs. 6 and 7. The temperature dependent electron contribution to the pressure was derived from the results of the band calculations according to (13). It appears to be very small in comparison with the phonon contribution (50 times smaller at the temperature 295 K). The resulting equation of state for Ir at different temperatures is presented in fig. 8. The results for Rh are similar and not presented here. Unfortunately, at present we have no experimental data to be compared with the above results.

§5. Elastic moduli at high pressures

Information about the behavior of the Ir and Rh lattice properties at different pressures can be obtained in the framework of the simple pseudopotential model used here. The extraction of such information from experiments seems today to be difficult. Therefore, we present the results of the corresponding calculations for Ir (fig. 9). The results for Rh are similar.

§6. Conclusion

The reasons why the lattice properties of Ir and Rh are so succesfully described in the framework of the used simple pseudopotential model are not fully understood. However it is believed that if not sufficient, then at least necessary condition for this is the absence of any noticable singularities in the density of electron states in the immediate vicinity of E_F. The results of the calculations made by us at different pressures (figs. 10,11) show that at not too high pressures this remains the feature of Ir, and, what's more, the character of the electron structure near E_F is unchanged. Therefore, it

can be assumed that whatever the reason for the succesful pseudopotential description at $p = 0$, the situation at high compressions will not be too different from that at $p = 0$. As a result, one can expect that the information about the lattice properies of Ir (and its analogue Rh) at $p \neq 0$ which was derived from the pseudopotential calculations appears ot be raliable.

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Table 1. The values of the phonon frequencies $\omega(\mathbf{q})$ and the microscopic Gruneisen parameters $\gamma(\mathbf{q})$ in the simmetric points points of the Brillouin zone for Ir and Rh. $\omega(\mathbf{q})$ in THz. A-H stands for the values calculated with the Animalu-Heine pseudopotential, I stands for the values calculated with the addition proposed in I.

Table 2. The contribution of the zero point vibration to energy and pressure for Ir and Rh. A-H stands for the values calculated with the Animalu-Heine pseudopotential, I stands for the values calculated with the addition proposed in I.

Fig. 1 Microscopic Gruneisen parameters for Ir calculated for the pseudopotential from Ivanonv *et al* 1994 (dashed line) and from I (solid line).

Fig. 2 Microscopic Gruneisen parameters for Rh calculated for the pseudopotential from Ivanonv *et al* 1994 (dashed line) and from I (solid line).

Fig. 3 Temperature dependence of the linear coefficient of thermal expansion (a) and the macroscopic Gruneisen parameter (b) for Ir. Dashed line - calculation for the pseudopotential from Ivanov *et al* 1994; solid line — calculation for the pseudopotential from I. $\diamond$ in fig. 3a — experiment from Korenovsky and Polyakova, 1990. $T_{pl} = \hbar\omega_{pl} = \hbar(4\pi Z e^2/M\Omega_0)^{1/2}$, ω_{pl} is the ionic plasma frequency.

Fig. 4 Temperature dependence of the linear coefficient of thermal expansion (a) and the macroscopic Gruneisen parameter (b) for Rh. Dashed line — calculation for the pseudopotential from Ivanov *et al* 1994; solid line — calculation for the pseudopotential from I. $\diamond$ in fig. 4a — experiment from Korenovsky and Polyakova, 1990. $T_{pl} = \hbar\omega_{pl} = \hbar(4\pi Z e^2/M\Omega_0)^{1/2}$, ω_{pl} is the ionic plasma frequency.

Fig. 5 Equation of state for Ir at $T = 0$. Solid line — calculation for the pseudopotential from I; $\diamond$ — *ab initio* calculations.

Fig. 6 Dependence of the phonon contribution to pressure upon volume at $T = 295K$ and $T = T_m$ for Ir (solid line) and Rh (dashed line). The calculations were made for the pseudopotential from I.

Fig. 7 Temperature dependence of the phonon contribution to pressure for Ir (solid line) and Rh (dashed line). The calculations were made for the pseudopotential from I. $T_{pl} = \hbar\omega_{pl} = \hbar(4\pi Z e^2/M\Omega_0)^{1/2}$, ω_{pl} is the ionic plasma frequency.

Fig. 8 Equation of state for Ir at T=295 K and $T = T_m$. $\diamond$ is *ab initio* calculation of p_0 with pseudopotential calculation of p_{ph} using the addition proposed in I at temperature 295 K. $\circ$ is the same at the temperature $T = T_m$. Solid line — all quantities were calculated with the pseudopotential proposed in I, temperature is 295 K. Dashed line — the same at the temperature $T = T_m$.

Fig. 9 Dependence of the elastic moduli B_{ik} on volume for Ir. The calculations were made for the pseudopotential from I.

Fig. 10 The density of electron states (a) and the electron energy spectrum (b) in Ir at equilibrium volume.

Fig. 11 Density of electron states in Ir at different pressures.

table 1

	$\omega(\mathbf{q})$			$\gamma(\mathbf{q})$		
	(1,0,0)	(1,1/2,0)	(1/2,1/2,1/2)	(1,0,0)	(1,1/2,0)	(1/2,1/2,1/2)
Ir A-H	8.06	7.00	8.11	2.39	2.27	2.33
	5.65	5.85	4.03	2.18	1.83	1.60
Ir I	6.98	5.90	7.44	2.90	3.01	2.55
	5.16	5.22	4.01	2.89	2.17	1.72
Rh A-H	10.03	8.63	9.97	2.17	2.10	2.15
	7.04	7.10	4.91	1.99	1.68	1.44
Rh I	7.62	6.08	8.51	3.12	3.76	2.51
	5.93	5.64	4.86	3.34	2.37	1.64

table 2

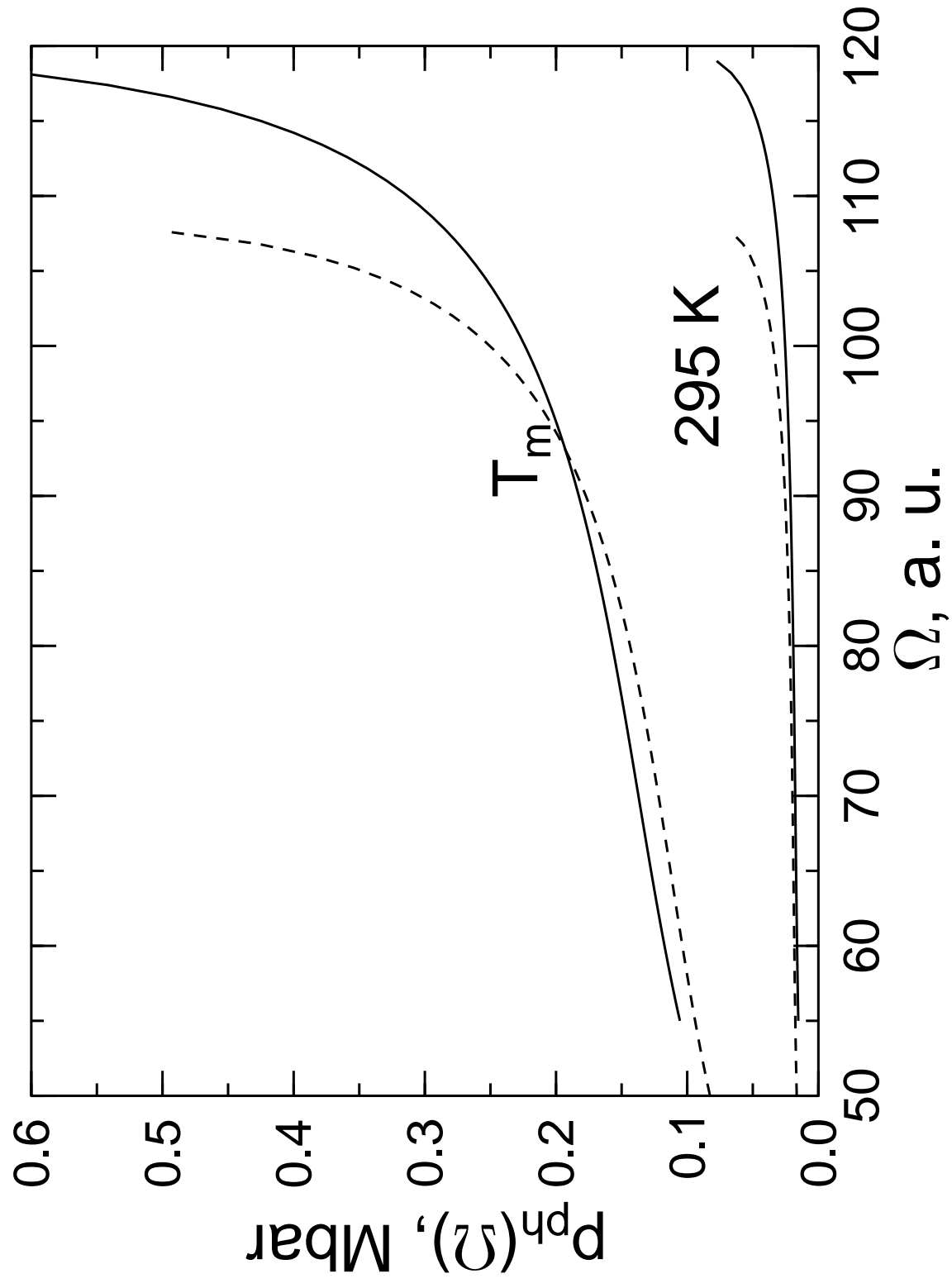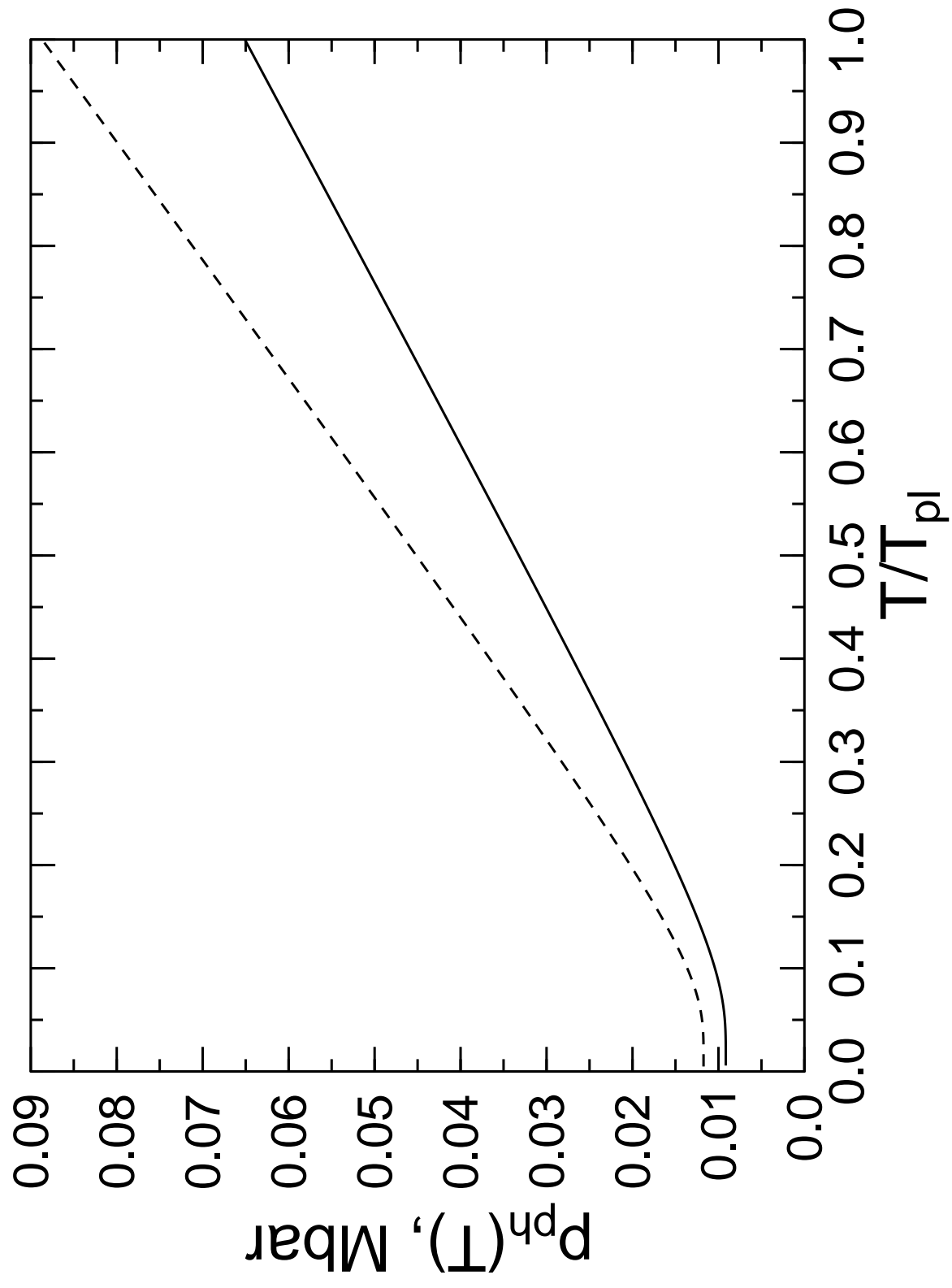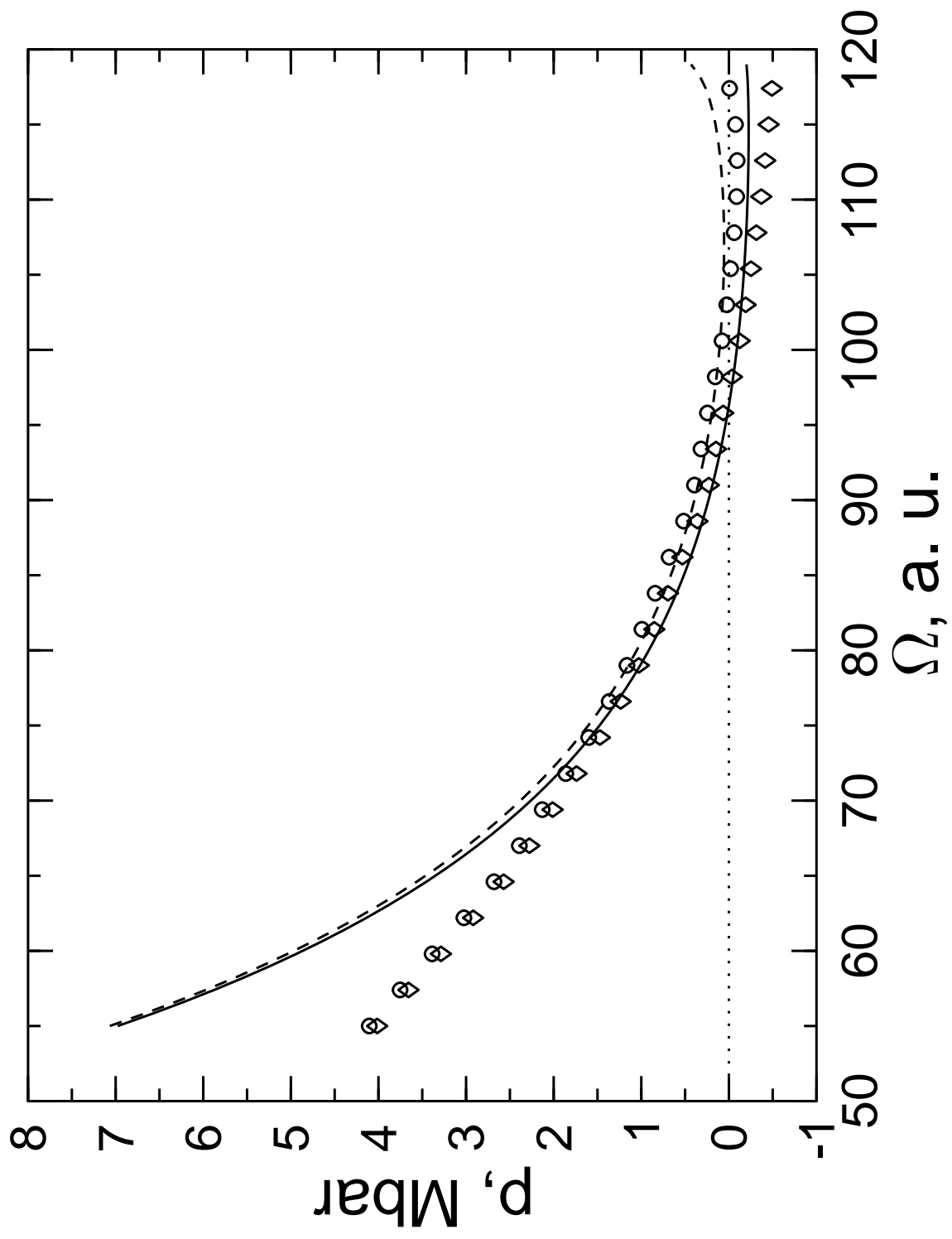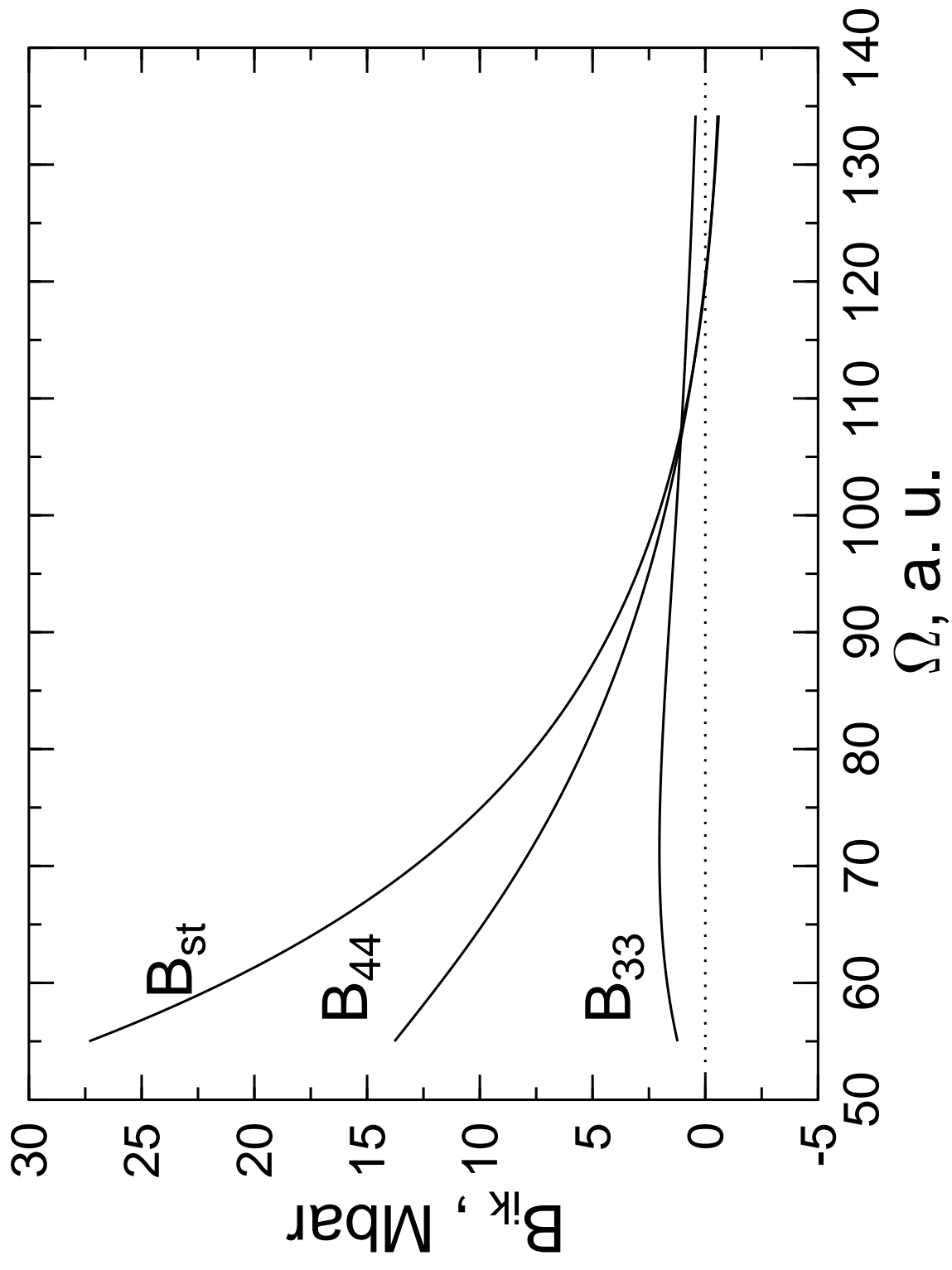|	Ir A-H	Ir I	Rh A-H	Rh I
$E_{zp}/E_0 10^4$	2.49	2.53	4.54	3.78
$P_{zp}/P_0 10^3$	2.63	3.1	3.77	5.25

E N E R G Y
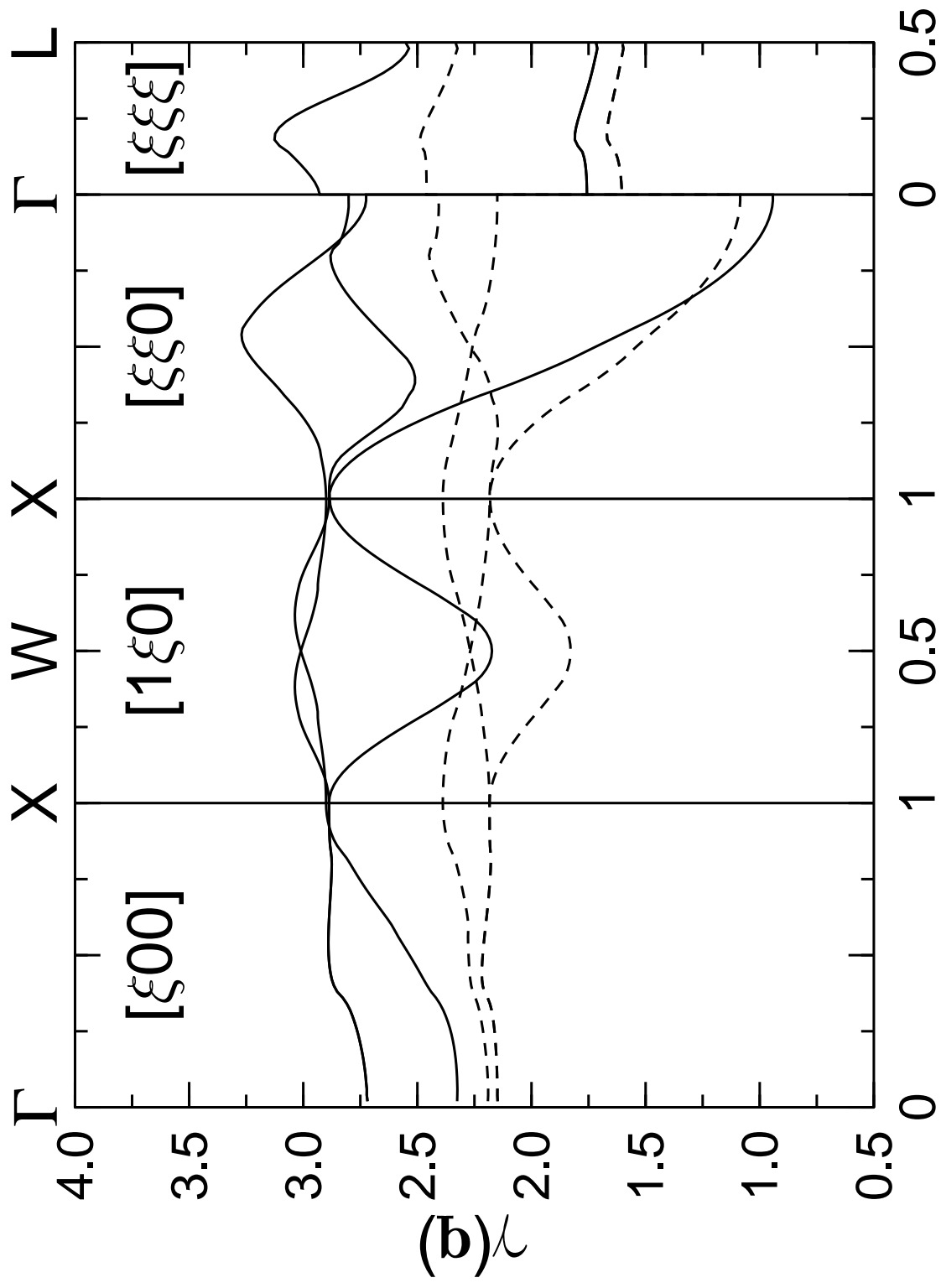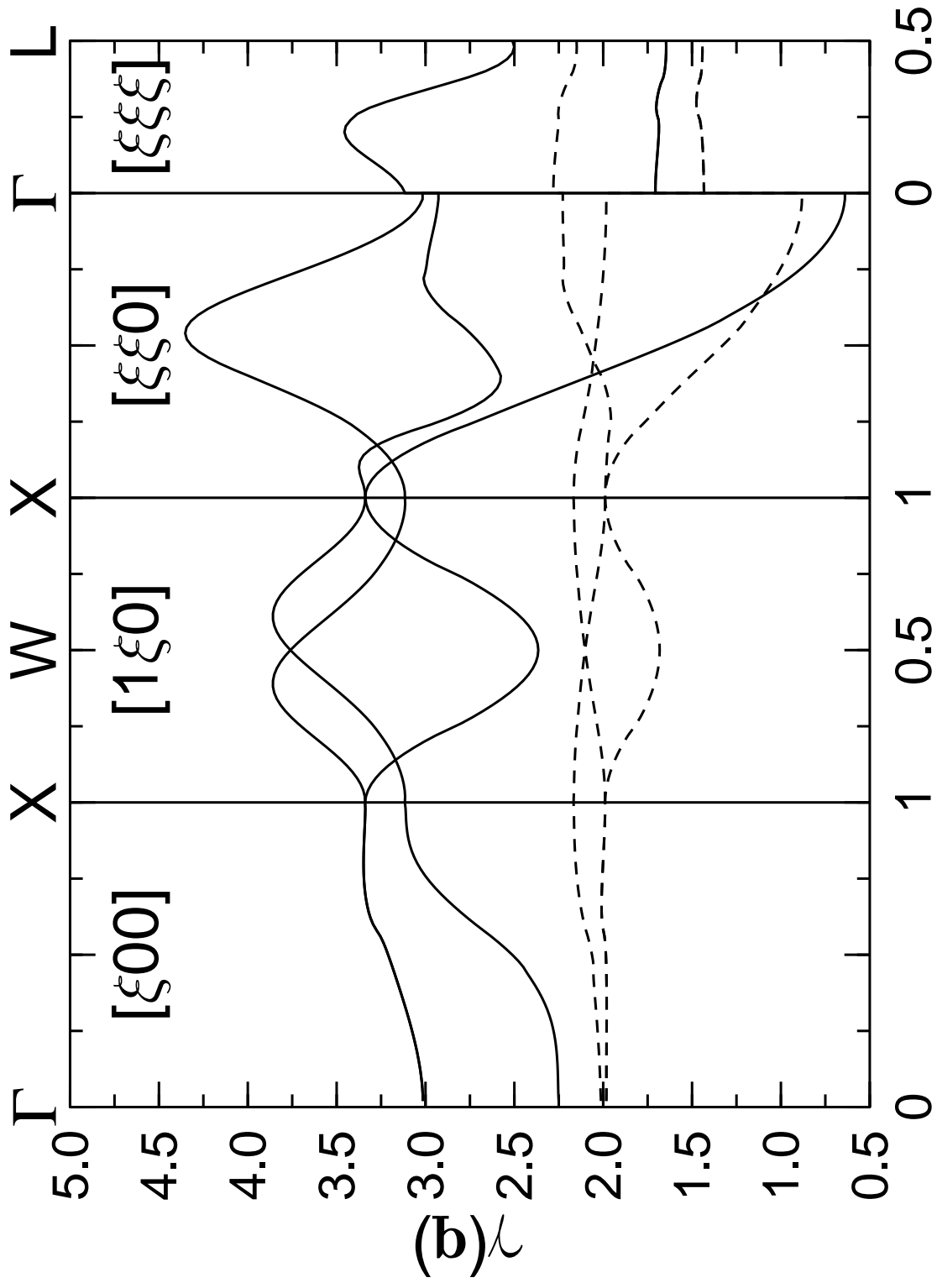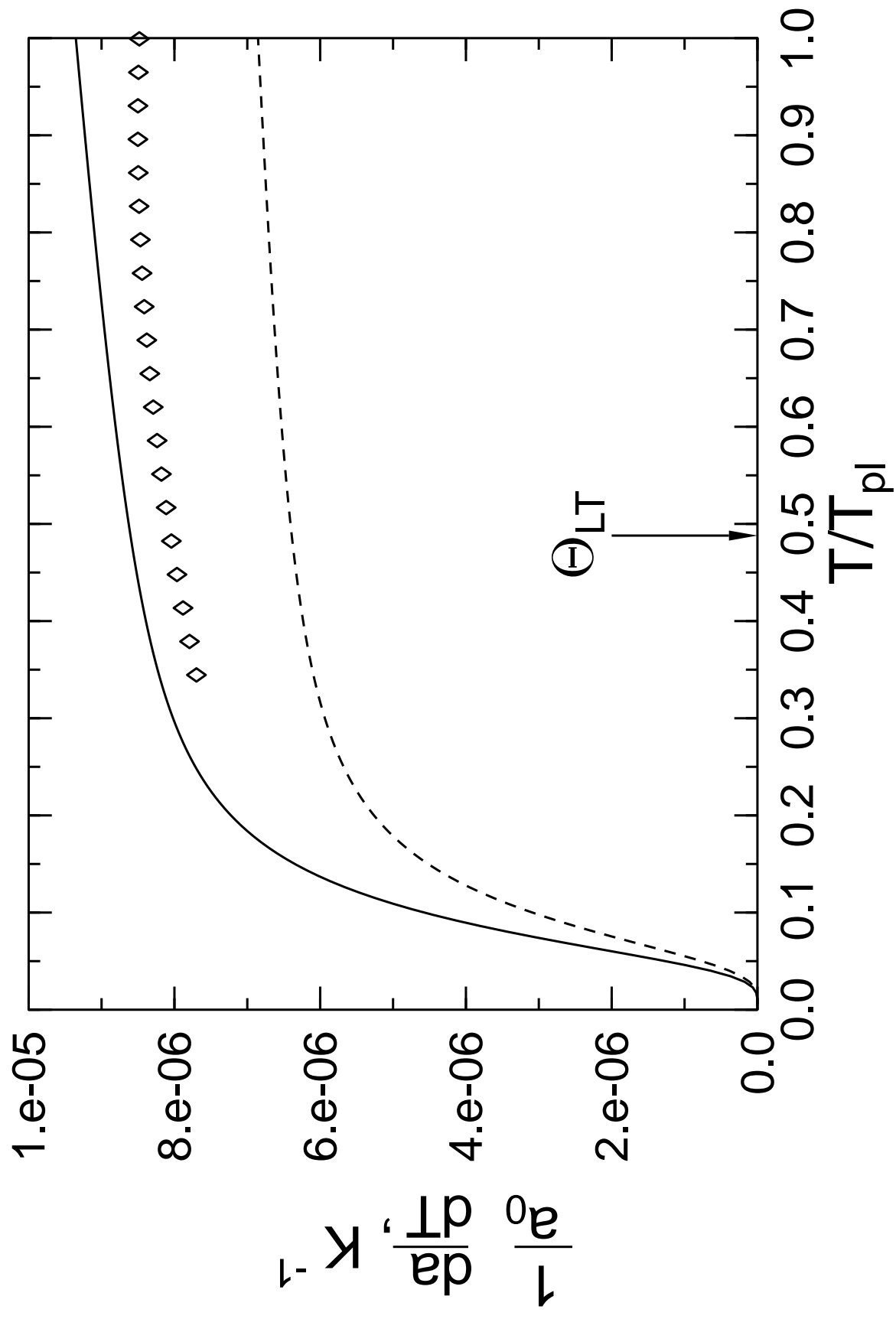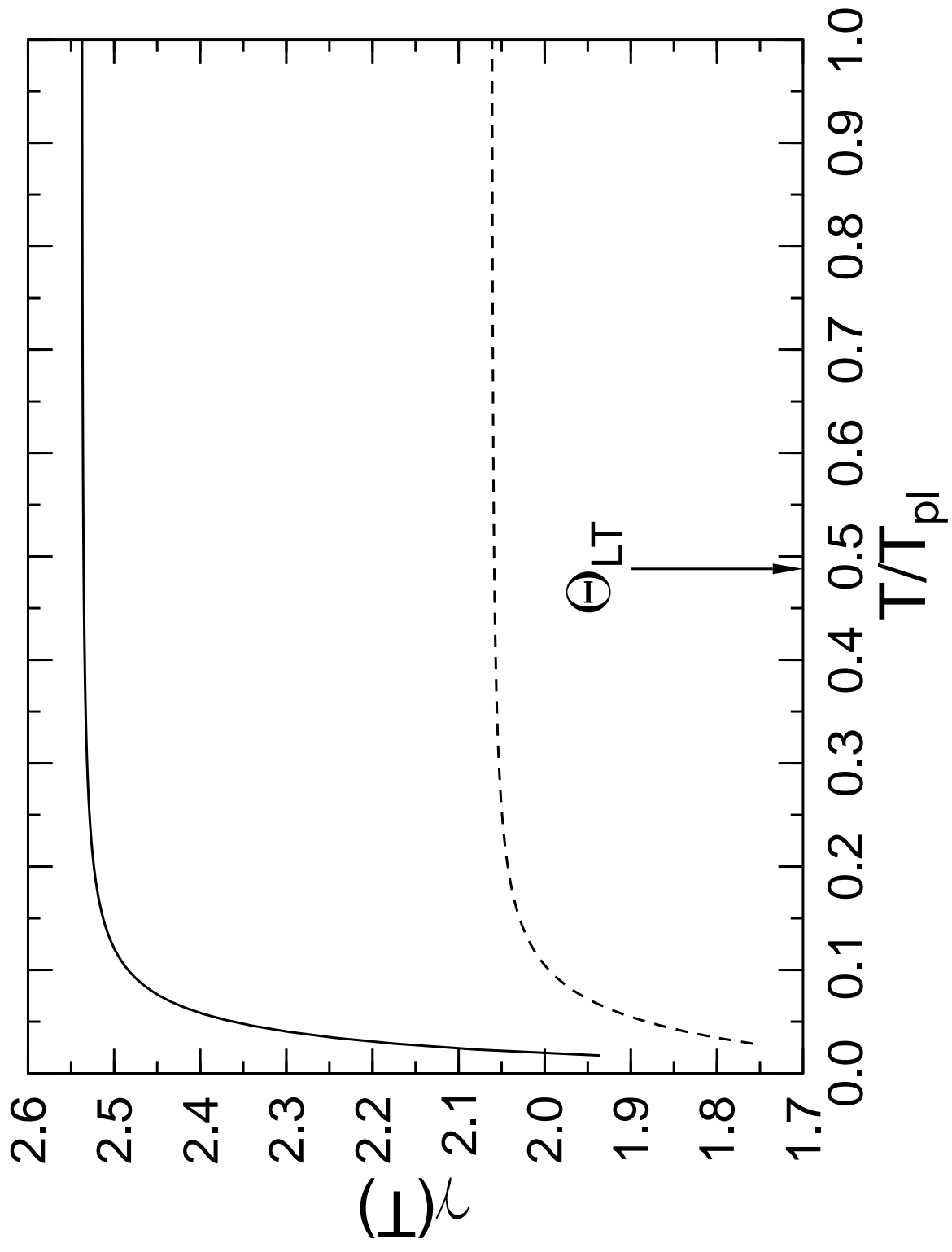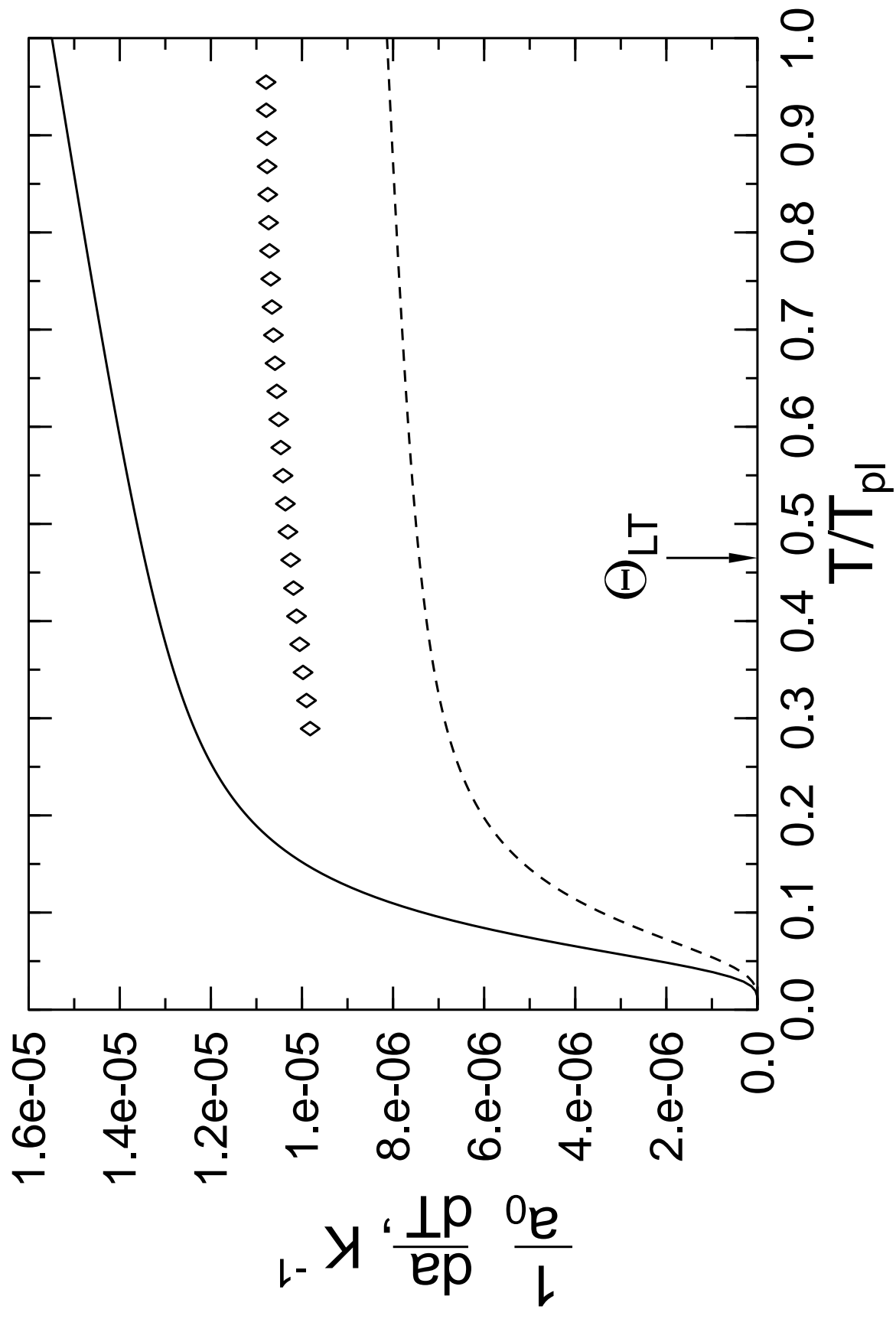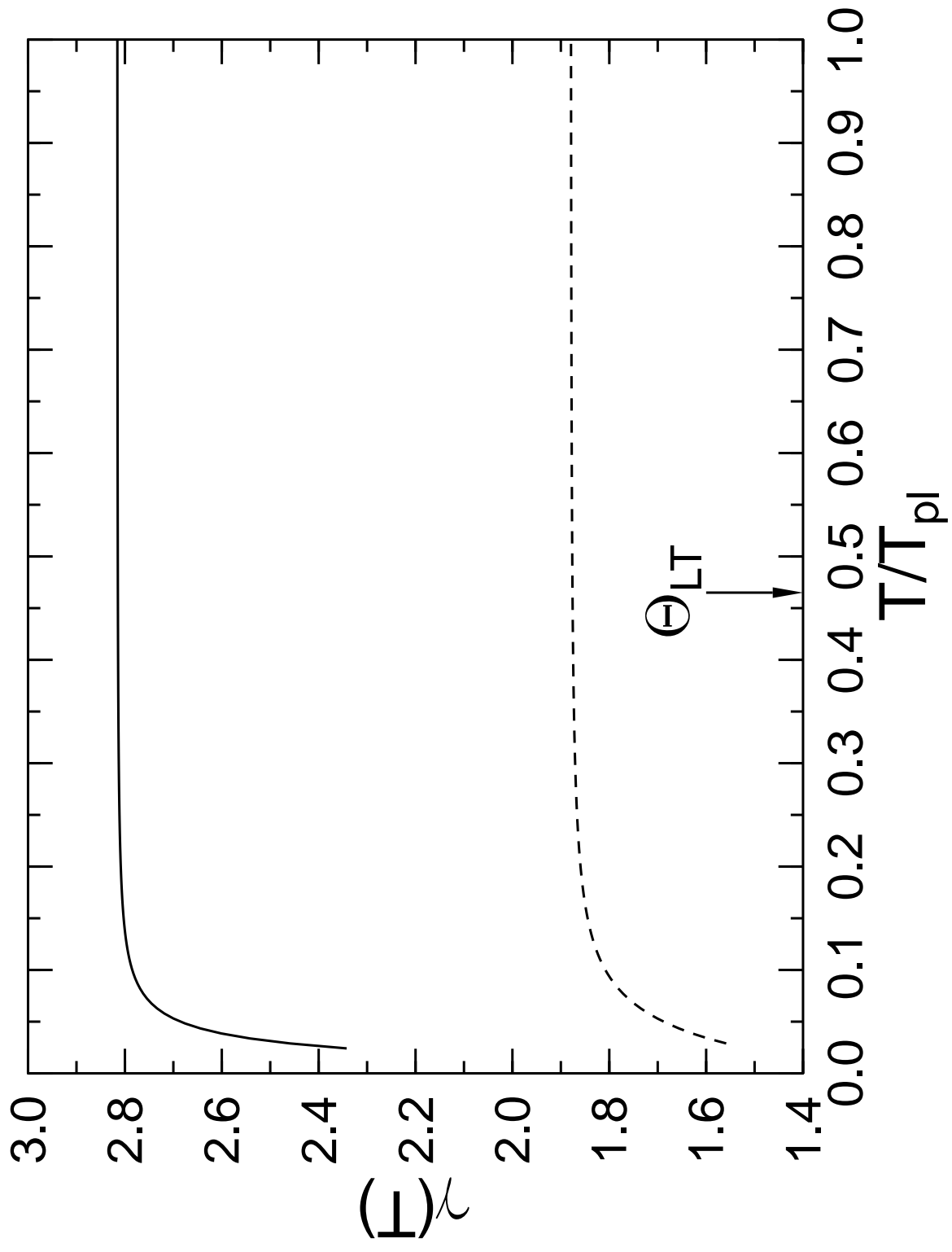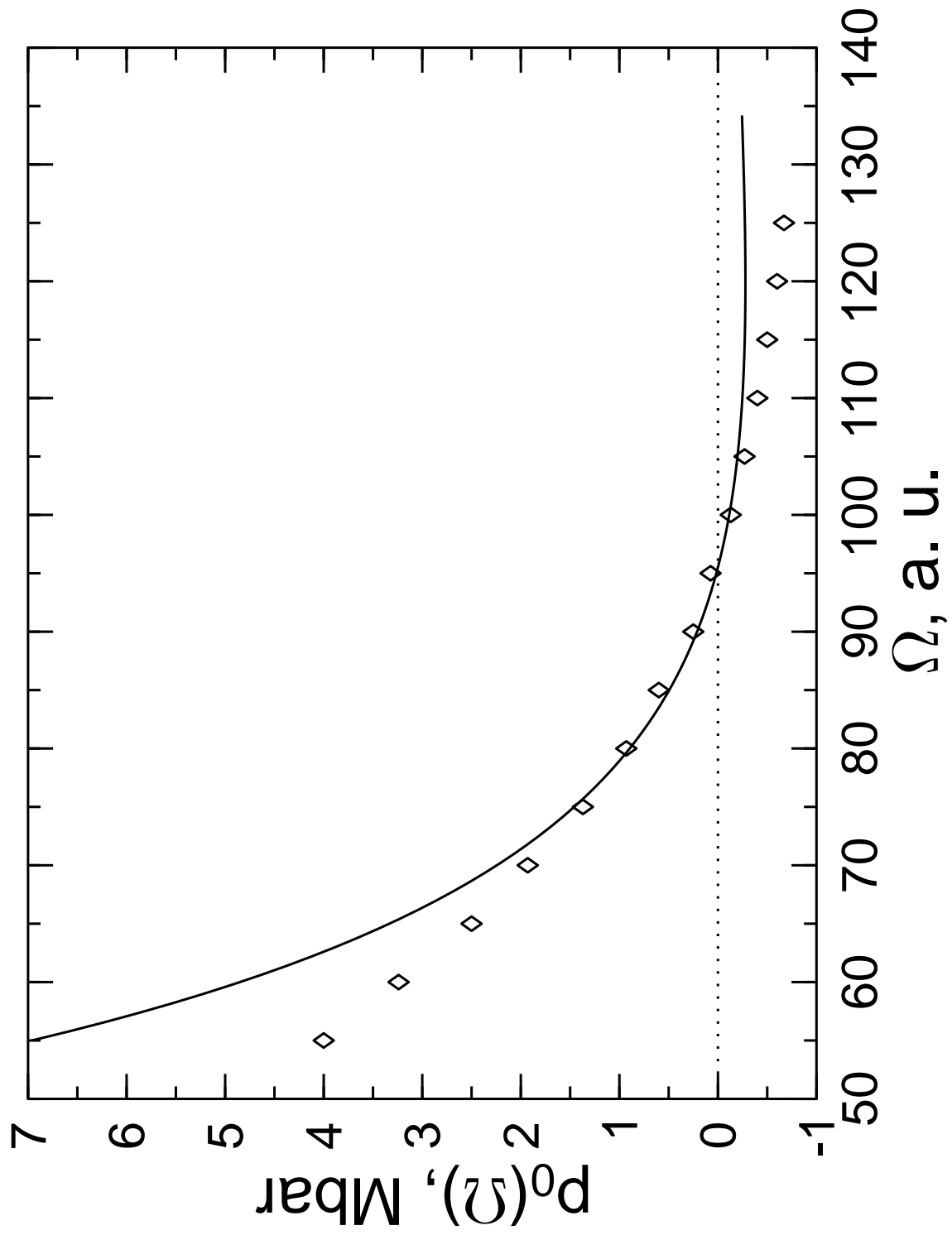
Ir (fcc) Lattice constant: 7.30

(a) Ir fcc 7.1

(b) Ir fcc 6.9